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TECHNICAL MEMORANDUM No. 13/M/67

Investigations of Crystal Modification of Urea

R.J.E. Williams

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by

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1. SUMMARY

Modification of the crystal habit of urea by crystallisation from water in the presence of additives, and from a wide range of organic solvents has been investigated. Addition compounds of urea with alicyclic ketones, hitherto unreported, have been discovered. The favourable physical properties of these addition compounds ~~have been~~ found to make them suitable intermediates in the preparation of urea in a free-flowing, non-caking form. The parameters for the laboratory manufacture of this type of urea have been examined as a basis for a large-scale continuous process. Provisional patent action has been taken. An investigation into the possible use of this type of urea as a host for the selective absorption of certain organic solvents has ~~been~~ made.

2. INTRODUCTION AND OBJECT OF INVESTIGATION

The crystallisation of urea from water or organic solvents has been studied as part of a general programme of examination of factors affecting the crystallisation of nitrogen containing compounds used as, or related to, secondary explosives. Earlier investigations (1,2) have shown how nitroguanidine, which may be considered to be derived from urea, can be recrystallised from water in a free-flowing, high bulk density form by batchwise or continuous spraying methods. Other studies, to be reported, have been made on the modification of PETN, tetryl, RDX and HMX by crystallisation from organic solvents with, in some cases, the incorporation within the crystals of particulate inert materials to give modification of explosive properties.

In the case of urea, discussions with the National Research Development Corporation have indicated that a process for the preparation of the compound in a free-flowing, non-caking form would have great industrial value. In modern manufacturing processes urea is crystallised from solution in water as a poor flowing material due to the high length/breadth ratio of the crystals and to a tendency to cake badly on bulk storage. For large-scale fertilizer applications these are serious disadvantages and a further treatment is given to yield a free-flowing form. This treatment, known as prilling, involves melting the crystalline urea and cooling the melt by spraying down a high tower to give rounded granules. The process, however, suffers from the disadvantage that at the temperature required for melting urea (m.p. 132.7°C) some decomposition of the compound takes place with formation of biuret in proportions which would be harmful to certain crops. In addition, the high capital cost of prilling plant and the thermal energy required to melt crystalline urea represent a considerable part of total manufacturing costs.

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In view of interest in a replacement for the prilling process it was thought that the most useful study from a practical viewpoint would be of crystallisation methods designed to give a free-flowing granular form of urea. Two general methods were decided upon: (a) recrystallisation from water with the use of additives as crystal modifiers, and (b) recrystallisation from solvents other than water.

3. EXPERIMENTAL

3.1 Crystallisation from Water

A control experiment in which 3 g urea was dissolved in 1.5 ml water at 70°C and cooled with agitation to ambient temperature gave a product consisting of matted and aggregated acicular crystals having a length/breadth ratio of approximately 7/1 (Fig. 1), poor flowing, and tending to cake in the dry state.

Similar experiments were carried out with the addition of materials which are known modifiers of crystal growth. The additives were dissolved in the hot solution at concentrations ranging from 0.1 to 1.0 per cent by weight on the urea present. The following additives were investigated:

Non-ionic, cationic and anionic surface active agents.
Anionic dispersing agents.
Methylcellulose.
Sodium carboxymethylcellulose.
Amylopectin glycollates.
Polyvinyl alcohol.
Gelatin.
Dextrin.
Fish-glue.
Ammonium sulphate, ammonium nitrate, ammonium chloride.
Nitric acid.
Colloidal graphite.
Acid magenta.
Phenol red.

Combinations of pairs of these additives were used, e.g. methylcellulose and surface active agents.

Practically no effect was observed in any experiment, the products being similar in appearance and properties to the control crystallisation, and it was concluded that this line of approach showed little promise of improvement in handling properties.

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3.2 Crystallisation from Organic Solvents

The solvents used could be divided into three groups as judged by the experimental results obtained:

(i) Solvents in which the solubility of urea was found to be too low for practical use.

(ii) Solvents which gave urea in a similar form to water-crystallised material.

(iii) Solvents which gave modification of crystal shape.

3.2.1 Solvents in which the Solubility of Urea was Found to be too Low for Practical Use

Petroleum ethers
n-Hexane
Cyclohexane
Dichloromethane
Chloroform
Carbon tetrachloride
Carbon disulphide
Monohydric alcohols above the propanols in homologous series
Glycerol triacetate
Derivatives of ethanediol where both hydroxyl hydrogens are substituted by alkyl groups
Aromatic hydrocarbons
Pyridine
Chlorobenzene
Nitrobenzene

3.2.2 Solvents which gave Urea in a Similar Form to Water-crystallised Urea

Methyl alcohol
Ethyl alcohol
1-Propanol
2-Propanol
Acetophenone
Methoxyethanol
Ethanediol
1:2 Propanediol
1:3 Propanediol
Glycerol
Glycerol monoacetate
Glycerol diacetate

3.2.3 Solvents which gave Modification of Crystal Shape

Methyl acetate
Ethyl acetate
Allyl alcohol
Furfuryl alcohol
Diacetone alcohol
Benzyl alcohol
Cyclohexanol

Recrystallisation from these solvents gave urea crystals which tended to be pointed at one end and had a length/breadth ratio of approximately 2/1 (Fig. 2).

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In general, the solubility of urea in this group of solvents was found to be quite low, but in the case of diacetone alcohol the solubility ranged from 2 per cent at 20°C to about 10 per cent at 100°C, offering possible development of a process yielding free-flowing crystalline urea. However, this was not proceeded with because the simultaneous discovery of the urea/cyclohexanone adduct showed a means of obtaining urea in a granular form.

3.3 Adduct Formation

It was found that urea readily forms addition compounds, or adducts with cyclopentanone or cyclohexanone. These adducts consist of regular prisms (Fig. 3) which, on drying at 60° - 80°C, readily evolve the included cyclic ketone giving urea in a granular, free-flowing, rather friable form.

Cyclohexanone is less expensive and more readily available than cyclopentanone and it was decided to concentrate upon the cyclohexanone adduct in the development of a method for the production of the desired form of urea.

3.3.1 Urea/Cyclohexanone Adduct

Preliminary analysis showed the adduct to contain cyclohexanone approximately 36 per cent by weight.

A method based on the formation of the adduct by cooling a hot solution of urea in cyclohexanone would require a large throughput of solution per unit mass of product because of the relatively low solubility of urea in cyclohexanone at temperatures low enough to preclude the formation of biuret. A number of experiments were tried involving the use of mixtures of cyclohexanone and methylated spirit to increase the solubility of urea and the following is an example of a method evolved.

150 ml of a mixed solvent consisting by volume of 2 parts of cyclohexanone and one part of methylated spirit are saturated with urea at 30°C. The resulting solution is stirred and cooled to just below 20°C to yield crystalline particles of the adduct. Stirring is continued and to this base solution is added in a steady stream urea dissolved in the mixed solvent at 60°C in the proportion of 36 g urea/450 ml solvent. The temperature of the mixture is maintained at 20° - 25°C during the addition by means of external cooling and when the addition has been completed the adduct is separated by filtration. It is dried at 60° - 80°C to remove residual methylated spirit and cyclohexanone together with included cyclohexanone.

/A .....

A similar product may be obtained by the low pressure distillation of methylated spirit from a solution of urea in the mixed cyclohexanone/methylated spirit solvent.

In a further series of experiments it was observed that when cyclohexanone was added to a hot solution of urea in water and the mixture stirred with external cooling, the adduct was readily formed and could be separated and dried as in the above example. A process based upon the use of a hot solution of urea in water would be particularly advantageous since in the final stages of manufacture such a solution is obtained.

A series of experiments was undertaken to establish the optimum conditions for such a process and, initially, saturated solutions of urea in water at various temperatures were treated with excess cyclohexanone and cooled, with stirring, to $20^{\circ}C$. It was found that solutions saturated with urea at temperatures above $65^{\circ}C$ tended to deposit urea in addition to the adduct unless the cooling was allowed to take place over long periods, e.g. in air. However, solutions saturated at temperatures below $65^{\circ}C$ and cooled fairly quickly by external cold water circulation deposited no urea, either during or after cooling, the adduct alone being formed.

Having established the maximum permissible initial temperature for crystallisation to be of the order of $65^{\circ}C$ a further series of experiments was undertaken to correlate product yield with the volume of cyclohexanone used. Various amounts of cyclohexanone were added to saturated solutions of urea in water at $60^{\circ}C$, the mixtures cooled with stirring to $20^{\circ}C$ and the products dried and weighed to give the yield of urea. These experiments showed that a 40 per cent deficiency of cyclohexanone, i.e., 40 per cent less than the calculated quantity required to precipitate all the urea present as adduct, resulted in no adduct formation at all, the product crystallising on cooling being urea in its usual form. The use of quantities of cyclohexanone ranging from a 40 per cent deficiency to 25 per cent excess gave adduct formation on cooling, with yields of up to 90 per cent of the original weight of urea taken, after filtration and drying to remove included cyclohexanone. The variations in yield were found to be directly proportional to the volume of cyclohexanone used. Increasing the excess by more than 25 per cent gave only fractional increase in final yield.

During the course of these experiments it was found that when cyclohexanone at ambient temperature was added to hot saturated solutions of urea, and the mixture immediately cooled by external water circulation, crystalline urea was often formed. Crystallisation of the adduct is accompanied by an increase in temperature, and to eliminate any possibility of formation of crystalline urea it was found to be necessary to delay the application of external cooling until the rise in temperature indicated that adduct formation had begun.

/Although .....

Although large-scale production would be continuous the following laboratory scale batch method illustrates a process which has been evolved from the foregoing experiments.

140 g urea are dissolved in 56 ml water and the temperature adjusted to 62°C, (saturated solution at 60°C). The solution is stirred and 120 ml cyclohexanone added, the base temperature being allowed to fall to 55° ± 1°C at the end of the addition which may be as rapid as can be conveniently achieved. The mixture is stirred until the adduct begins to form with an accompanying rise in temperature; this usually occurs within two to three minutes. It is then cooled to 20°C with continued stirring and the product separated at the vacuum pump. The adduct is then heated in the oven or on a hot-table at 70° - 80°C to eliminate residual mother liquor and included cyclohexanone. The final product may be easily passed through a 5 BSS or 10 BSS sieve to give urea in the form of free-flowing, non-caking granules. Yield 120 g (Fig. 4).

In order to obtain information on the composition of mother liquors from a process of this type, solutions of urea in water at different known concentrations were treated with a slight excess of cyclohexanone at 20°C. The volume of cyclohexanone which dissolved was noted and the density of the lower urea/cyclohexanone/water solution was determined. Under these conditions the relative solubility of urea and water in the upper layer of cyclohexanone was small enough to be disregarded in the analysis of the results which were plotted on a graph (Fig. 5). The curve shows that the solubility of cyclohexanone in urea solutions increases with increase in the concentration of urea until the point is reached where the concentration of urea is sufficiently great to give adduct formation.

In the case of the laboratory method detailed above determination of the density of the mother liquor, followed by reference to Fig. 5, showed that it contained 40 per cent w/v urea and 15 per cent v/v cyclohexanone, which, since the adduct had been removed at 20°C, was in accordance with the experimentally determined result.

3.3.2 Adducts with Other Organic Compounds

It has previously been mentioned that cyclopentanone which forms a similar adduct with urea to that given by cyclohexanone, could be used as an alternative modifying agent and it was decided to examine other organic solvents for possible similar use.. A standard method of test for adduct formation was used: 20 ml of a solution of urea in water, saturated at 10°C, was stirred at 20°C and 20 ml of the test compound added. The resultant mixture was cooled to 10°C and stirred for one hour. Under these conditions both cyclopentanone and cyclohexanone readily gave adducts. The following results were obtained:

/Adduct .....

Adduct formed with:	No adduct formed with:
Acetone	Sextone B (Methyl cyclohexanone)
Methyl ethyl ketone	2-Methyl cyclohexanone
Diethyl ketone	iso-Propyl methyl ketone
Methyl n-propyl ketone	Mesityl oxide
Methyl n-butyl ketone	Cyclopentanol
Ethyl n-propyl ketone	Cyclohexanol
n-Hexanol	Aliphatic alcohols lower than hexanol
n-Octane	n-Heptane
Tetrahydrofuran	Cyclohexane
	Cyclohexene
	Benzene
	Pyridine
	Diethyl ether
	Diallyl ether
	Methyl acetate
	Ethyl acetate

When adducts were formed the crystals were invariably elongated and rather similar in appearance to urea itself or even more acicular in shape. On elimination of included adduct forming compound by heating, the resultant urea showed no improvement in flowing or non-caking properties over urea obtained by crystallisation from water.

3.3.3 Analysis of Urea/Alicyclic Ketone Adducts

Determination of the ketone content of the urea/cyclopentanone and urea/cyclohexanone adducts was made in two ways: (a) A sample of the adduct, wet with ketone was allowed to stand over adduct previously dried to eliminate all included ketone, and when the sample had attained constant weight signifying removal of extraneous ketone it was heated to constant weight at 80°C and reweighed to give the mass of residual urea; (b) The adduct was heated at 80°C until all ketone was eliminated. A weighed sample was then allowed to stand over the ketone until constant weight was attained.

Adduct	Method	Ketone, % by wt.	Mole urea/Mole ketone	Mole urea/ketone carbon atom
Urea/cyclopentanone	a	30.7	3.2	0.63
	b	30.9	3.2	0.63
Urea/cyclohexanone	a	36.0	3.5	0.58
	b	36.3	3.4	0.57

/X-ray .....

X-ray diffraction examination showed that the products of crystallisation of urea in the presence of these ketones are new phases and that the residues after heating are the usual tetragonal form of urea; the residues are pseudomorphic with the original adducts. A more detailed study of the adducts themselves will be undertaken and reported on at a later date.

3.4 Absorption of Organic Solvents by Urea

It was thought that the special form of urea obtained from the adducts might have a tendency to absorb selectively particular organic solvents. To investigate this a simple test was devised in which samples of urea obtained from six different adducts and a sample of urea crystallised from water, were allowed to stand with a dish containing the solvent in a closed vessel, at room temperature.

Full results are given in Table 1, but in general it was found that urea obtained from the cyclohexanone adduct was the most effective absorbent, although little absorption was obtained with any of the solvents tested except in cases where new adducts were formed.

The quantities absorbed were found to vary with variations in ambient temperature and the figures given in the Table are necessarily approximate only. Urea obtained from the adducts usually reached the stage of maximum absorption in a few days while urea crystallised from water often required several weeks for maximum absorption or adduct formation.

The absorbed materials were completely evolved when the samples were allowed to stand for a few hours in the open at room temperature.

4. DISCUSSION

4.1 Structure of the Adducts

During recent years much has been published on urea adduct formation and great interest has been shown in industry, particularly in the field of petroleum chemistry, in the ability of urea to form crystalline channel inclusion compounds with straight chain aliphatic molecules having a certain minimum number of carbon atoms. Adduct formation of this nature has been reported with hydrocarbons, alcohols, ethers, aldehydes, ketones, organic acids and esters, as long as the carbon chain is of a definite minimum length, which depends on the chemical nature of the compound, and unbranched, or with only a small branch relative to the chain length. It has always been believed that cyclic organic compounds would not form adducts with urea, and no reported instances of such

/formation .....

formation have been found in the literature, with the exception of compounds such as octadecyl benzene which has a long straight chain attached to the cyclic part of the molecule.

A review with 87 references (3) published in 1955 specifically excluded cyclopentanone and cyclohexanone from those compounds which form adducts with urea. An extensive literature search, which included a review with 79 references (4) published in 1963, has failed to find any reference to the ability of urea to form adducts with alicyclic ketones.

X-ray examination shows that urea crystallises in the tetragonal form and that its adducts are usually hexagonal (5,6,7). In these adducts the urea molecules build up in the unit cell in a helical way giving a central channel which is about 6 Å* in diameter at its widest part and in which the straight chain molecules rest end to end. Straight chain hydrocarbons have a cross-section of about 4.1 Å and readily form adducts whilst hydrocarbons with a single methyl branch require a channel diameter of 5.5 Å and only form adducts if the straight chain is of sufficient length. Benzene has a cross-section of about 5.9 Å and does not form an adduct. Cyclohexanone has a cross-section of about 5.5 Å and that of cyclopentanone is rather less, so these compounds may be considered border-line cases in tendency to form hexagonal adducts with urea.

It has been calculated (8) that in the hexagonal adducts each carbon atom in the straight chain aliphatic molecules requires 0.7 mole urea, and this has been established by analytical results. In the case of the adducts formed with cyclopentanone and cyclohexanone analysis shows that each carbon atom requires about 0.6 mole urea. This difference may not necessarily rule out a hexagonal structure because a true comparison cannot be made between aliphatic and alicyclic molecules.

Preliminary examination of the alicyclic ketone adducts has indicated that they may not be hexagonal, and further investigation will be undertaken, and reported on, by Duke, Crystallography/SAI., ERDE.

4.2 Recovery of Cyclohexanone

In any production process based on the urea/cyclohexanone adduct an important feature would be the recovery cycle for cyclohexanone. It would be comparatively simple to recover ketone eliminated from the adduct during the drying and decomposition stage but, as Fig. 5 shows, a significant quantity of cyclohexanone is retained in solutions of urea.

/This .....

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*1 Å = 10^{-10} m

This, of course, points to the association of urea and cyclohexanone in solution. The economics of a production method might call for cooling of solutions to temperatures below 20°C, but adjustment of mother-liquor temperature to 20°C followed by determination of the density and reference to Fig. 5 would give the concentrations of urea and cyclohexanone present. The liquor could then be returned to the adduct formation stage of the process after enrichment with solid urea or a hot concentrated solution of urea in water; thus no separation of cyclohexanone would be necessary. On the other hand it might be economically more feasible to distil off water from the mother liquor, at reduced pressure, to prevent decomposition of urea with the formation of biuret, which would give a further crop of the adduct and also free cyclohexanone.

Fig. 6 is an outline flow sheet for a possible continuous process.

5. CONCLUSIONS

5.1 The crystal habit of urea can be changed very little by crystallising from water in the presence of many substances known to be favourable to crystal modification.

5.2 Crystallisation of urea from a small group of solvents, in particular diacetone alcohol gives appreciable reduction in particle length/breadth ratio with consequent improvement in flowing property.

5.3 A method for obtaining urea in a free-flowing non-caking form has been devised by making use of the urea/cyclohexanone adduct. A possible disadvantage of this form is that it is of a friable nature and might crumble on handling in bulk. The extent of such crumbling is difficult to assess on the basis of small quantities of the material.

5.4 By means of a suitable crystalliser a method for continuous large-scale production could be evolved. It would be necessary for arrangements to be made to collect cyclohexanone evolved during the drying and decomposition cycle and return it to the process.

5.5 At the low temperatures used in such a process the increase in biuret content of the product would be negligible.

5.6 In view of the possible wide commercial application of the cyclohexanone/urea process patent action has been taken to cover the improvements in urea manufacture given by methods of this type (9).

/5.7 .....

5.7 A limited investigation of the possible use of urea to absorb certain organic solvents has shown that with some aliphatic compounds absorption from the vapour phase occurs more rapidly with urea obtained from adducts than with urea crystallised from water. A more detailed study of the use of these forms of urea could be worthwhile in a specific case where the separation of one component from a mixture of solvents is required.

6. ACKNOWLEDGEMENTS

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/TABLE 1 .....

TABLE 1

Absorption of Organic Solvents by Urea

Solvent	Amount absorbed, % of			
	Urea from Cyclo-hexanone adduct	Urea from Cyclo-pentanone adduct	Urea from Diethyl ketone adduct	Urea from Methyl n-Propyl ketone adduct
Benzene, Toluene) Xylene, n-Hexane) Cyclohexane) Cyclohexene) Petroleum ether 80 - 100) Petroleum ether 100 - 120) Chlorobenzene, Nitrobenzene)				NEGLIGIBL
Cyclohexanol	4	12	2	2
Sextone B (methyl cyclohexanone)	2	N	N	N
2-Methyl cyclohexanone	2	N	N	N
Dichloromethane	2	N	N	N
Chloroform	6 (ADDUCT	40 FORMATION)	1	N
Carbon tetrachloride	N	N	N	N
Carbon disulphide	N	N	N	N
1:2-Dibromoethane	2	N	N	N
Dioxan (diethylene dioxide)	53	59	54	59 (ADDUCT FORMAT
Diethyl ether	7	N	N	N
Methyl acetate	25	6	4 (POSSIBLY	3 ADDUCT F
Ethyl acetate	20 (ADDUCT FORMATION)	N	N	N
Amyl acetate	N	N	N	N

N = NEGLIGIBLE

A

TABLE 1

Absorption of Organic Solvents by Urea

Amount absorbed, % of total weight						
Urea from Cyclo-hexanone adduct	Urea from Cyclo-pentanone adduct	Urea from Diethyl ketone adduct	Urea from Methyl n-Propyl ketone adduct	Urea from Ethyl n-Propyl ketone adduct	Urea from n-Octane adduct	Urea crystal-lised from water
			NEGLIGIBLE			
4	12	2	2	1	1	15
2	N	N	N	N	N	N
2	N	N	N	N	N	N
2	N	N	N	N	N	N
6 (ADDUCT FORMATION)	40 (ADDUCT FORMATION)	1	N	N	39 (ADDUCT FORMATION)	27 (ADDUCT FORMATION)
N	N	N	N	N	N	N
N	N	N	N	N	N	N
2	N	N	N	N	N	N
53	59	54	59 (ADDUCT FORMATION)	59	54	53
7	N	N	N	N	N	N
25	6	4	3 (POSSIBLY ADDUCT FORMATION)	6	11	7
20 (ADDUCT FORMATION)	N	N	N	N	N	N
N	N	N	N	N	N	N

N = NEGLIGIBLE

B

FIG. 1 UREA CRYSTALLISED FROM WATER
PHOTOMICROGRAPH x 75

FIG. 2 UREA CRYSTALLISED FROM DIACETONE ALCOHOL
PHOTOMICROGRAPH x 75

FIG. 3 UREA/CYCLOHEXANONE ADDUCT
PHOTOMICROGRAPH x 75

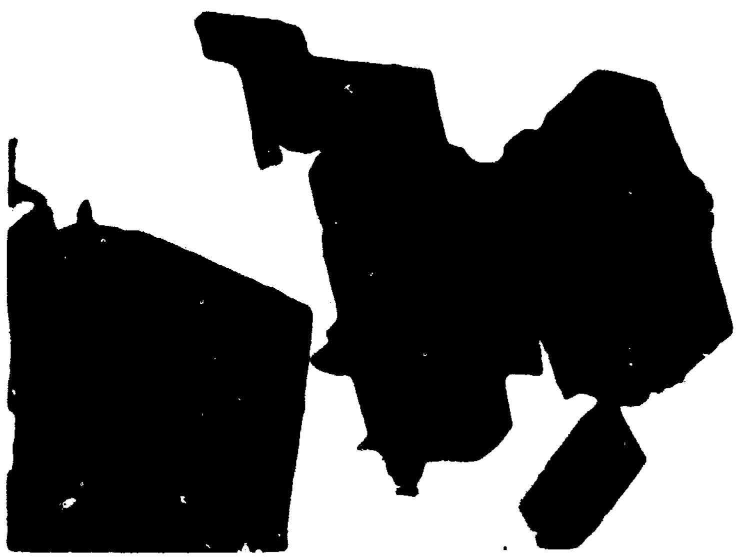

FIG. 4 ADDUCT AFTER HEATING TO REMOVE CYCLOHEXANONE
PHOTOMICROGRAPH x 75

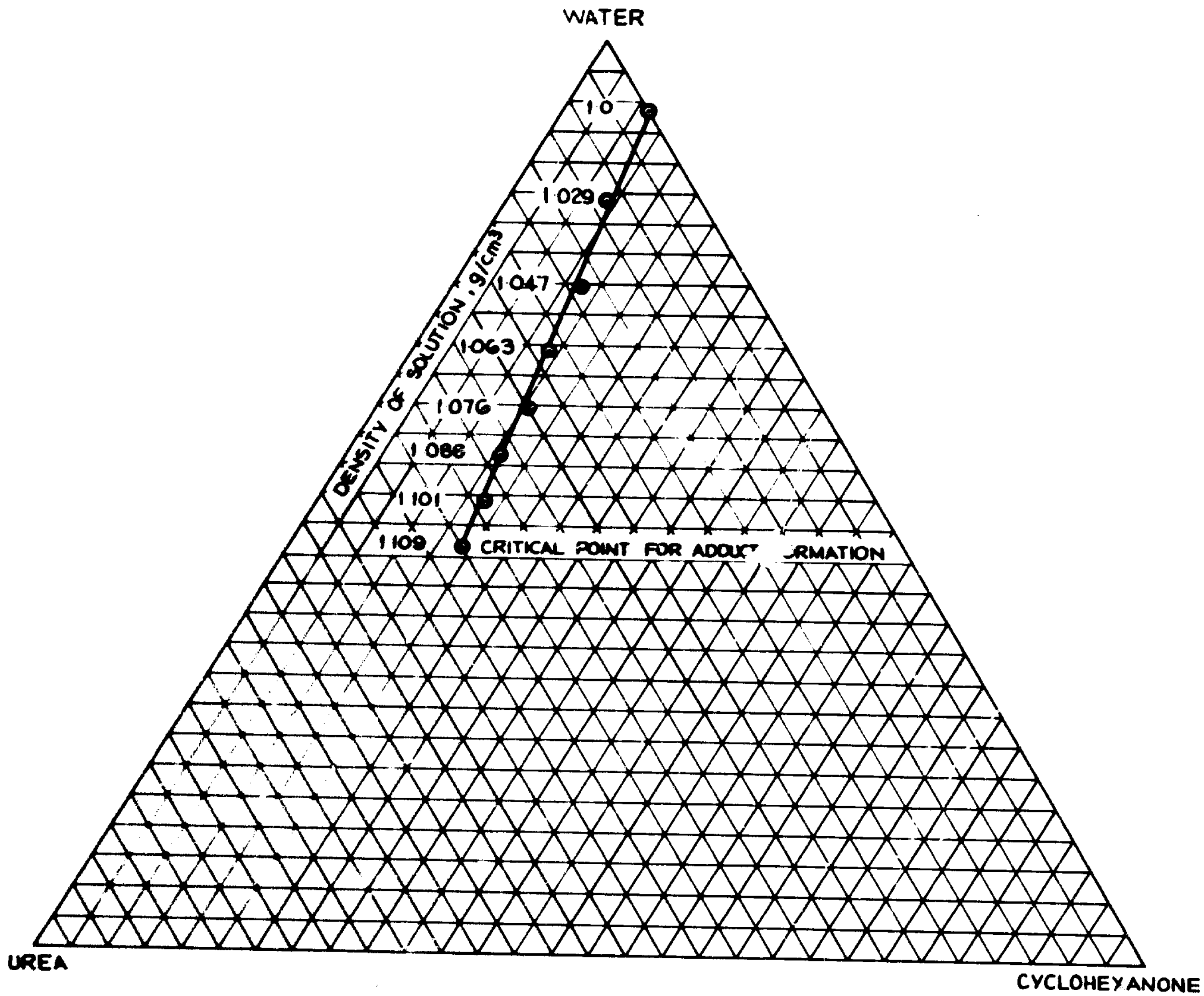

FIG 5 COMPOSITION OF THE UREA/CYCLOHEXANONE/WATER SOLUTION LAYER IN THE PRESENCE OF EXCESS CYCLOHEXANONE AT 20° C

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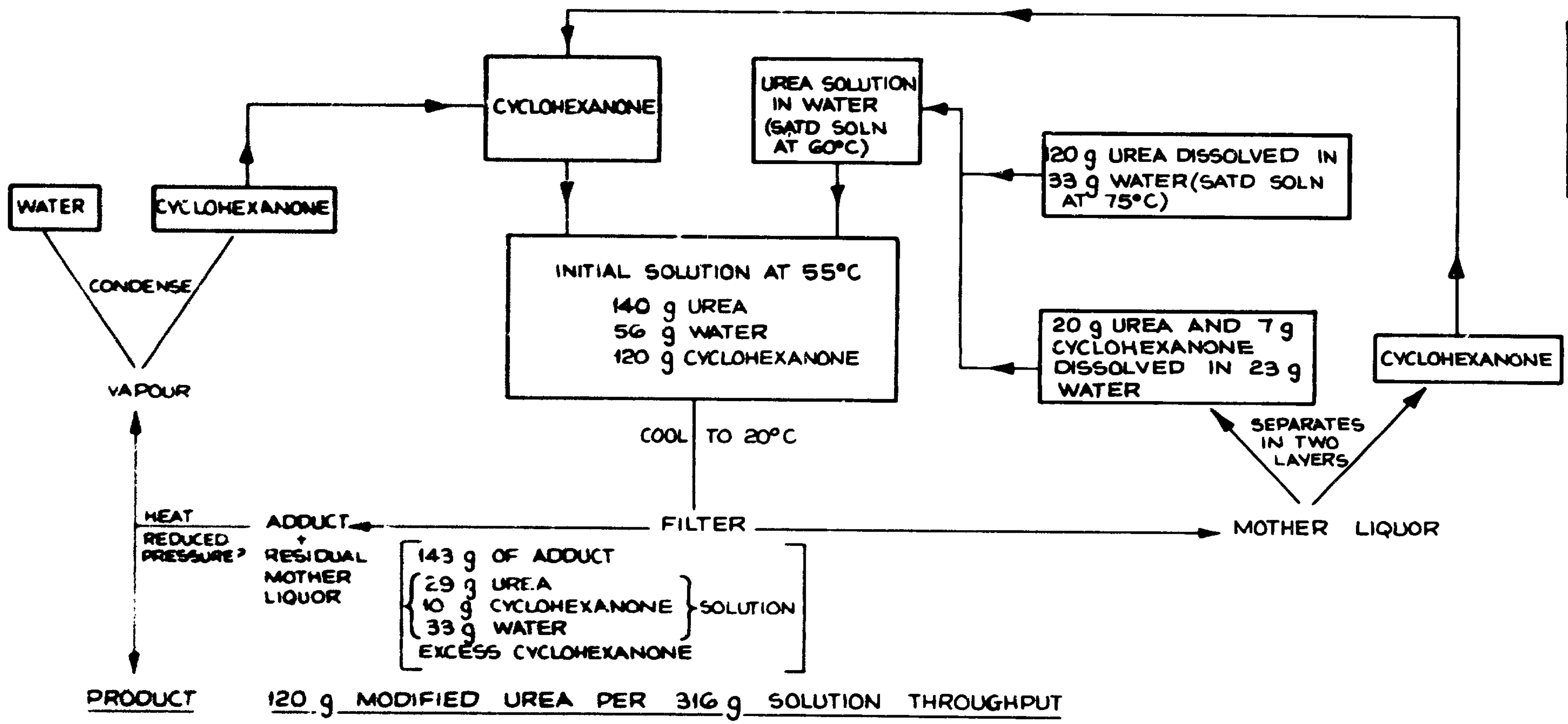

FIG 6 OUTLINE FLOWSHEET FOR A CONTINUOUS PROCESS BASED ON LABORATORY BATCHWISE METHOD

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